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Material-inherent data storage using magnetic magnesium-cobalt alloys

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Abstract

Magnetic magnesium alloys have an inherent load-sensitive behavior. These alloys are manufactured by casting of magnesium alloyed with the ferromagnetic element cobalt. In this context, the magnetoelastic effect can be used in order to measure mechanical loads during the component's service by means of a harmonic analysis of eddy current signals. The utilization of magnetic magnesium as a load-sensitive material in order to measure mechanical loads in structural components has been demonstrated in previous works. Another application is the magnetic labeling of the alloy. In this context the magnetic remanence is a significant characteristic value. A data track can be written directly on the material's surface by means of an electromagnetic write head. The track may contain relevant component-specific information like serial numbers, manufacture date and expected lifetime. This information can be read out by means of a sensor utilizing the giant magnetoresistive (GMR) effect. The magnetic labeling in relation to the manufactured alloy and the cooling rate during the casting process is examined in this work. The magnetic labeling of three alloys based on magnesium, cobalt and zinc has been investigated; these are MgCo4 and MgCo4Zn2. The alloys' mechanical as well as their magnetic properties are significantly influenced by these additional alloying elements. In order to investigate the alloys' suitability for magnetic data storage the quality of the data tracks read out using a GMR sensor are compared depending on the alloy composition. The magnetic labeling is influenced by the microstructure regarding solidification and cooling rate. A conical casting geometry with different solidification rates in top and bottom sections was used for an examination of the relationship between the density of the magnetic phases and the quality of the magnetic labeling.

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1. Introduction

Nowadays lightweight concepts become more important. Besides pure construction concepts, there is a great potential in the use of lightweight materials, such as magnesium alloys. These alloys have excellent specific strength and damping properties compared to steel or aluminum alloys. In order to monitor forces and stresses that are applied to structural components, a sensing element is required. A common technology to detect mechanical loads is the use of strain gauges that are applied to the component's surface. A major disadvantage of strain gauges is the necessary shielding against mechanical impacts. Moreover, conventional strain gauges allow the measurement of local strain only. Within the Collaborative Research Center 653, sub-project E2: "Magnetic Magnesium Alloys", load-sensitive magnetic magnesium alloys have been developed. These alloys' ferromagnetic properties enable an online-measurement of the mechanical loads using the harmonic analysis of eddy-current signals, which was shown in several previous studies [1-4]. Another application is the magnetic labeling in order to store relevant information, for example serial numbers or the experienced service time, directly on the magnesium component's surface.

In this work the quality of the magnetic labeling is investigated, depending on the alloy composition and the cooling conditions during casting.

Nomenclature

BSE	Backscattered electron contrast
Co	Cobalt
Cu-ETP	CW004A
EDX	Energy dispersive X-ray spectroscopy
GMR	giant magneto resistance
ICP-OES	Inductively coupled plasma optical emission spectrometry
Mg	Magnesium
N2	Nitrogen
SE	Secondary electron contrast
SEM	Scanning electron microscope
SF6	Sulfur hexafluoride
Zn	Zinc

2. Test methods

In this study, two alloys based on Mg, Co and Zn were manufactured by gravity die-casting. Due to the limited solubility of Co in solid Mg and the large melting point difference between Co and Mg, a special approach was necessary [2, 3]. The binary alloy MgCo4 and the ternary alloy MgCo4Zn2 were produced by gravity die casting using pure Mg as base material. Initially, 3 kg of pure Mg were melted in a boron-nitride coated steel crucible in a resistance-heated furnace at 730 °C. To prevent oxidation of the melt, a shielding gas mixture of N_2 and 0.3 % SF_6 was injected into the furnace's interior space. The alloying element Co was added to the pure Mg melt as an extruded powder rod, Zn was added pellet shaped. The powder rods consisted of 60 wt.% of pure Mg powder (Ecka non ferum Met.-pulver, < 71 µm, 99.8 %), blended with 40 wt.% of pure Co powder (Sigma Aldrich, 99.90 %, < 150 µm) by means of a powder mixer of the type MP-6 (Biomation, Jugenheim, Germany). After a mixing duration of 150 minutes, the powder mixture was compacted to extrudable billets using a cold-isostatic dry-bag pressing process, which was performed by the company Loomis Products (Kaiserslautern, Germany). These billets were extruded to rods with a diameter of 6 mm, which were dispensed into the Mg melt. By using such rods instead of loose powder the distribution of Co is improved because of reduced powder floating effects. After the alloying elements had been added, the melt was mechanically stirred for a period of 45 minutes at a stirrer's speed of 300 rpm. Afterwards the binary and ternary alloys were cast into a cone-shaped copper mold [3] made of Cu-ETP [5].

Due to the Cu-ETP's very large thermal conductivity (381 W/(m*K) at 200 °C) a rapid solidification was achieved generally. In detail, the conical geometry caused the highest cooling rates in the tip of the cone (6.9 K/s) and the lowest in the widest area of the cone (0.8 K/s) (see Fig. 1(b)). The calculated results using the casting simulation software MAGMA5 in Fig. 1(b) were based on AZ91 [2, 3].

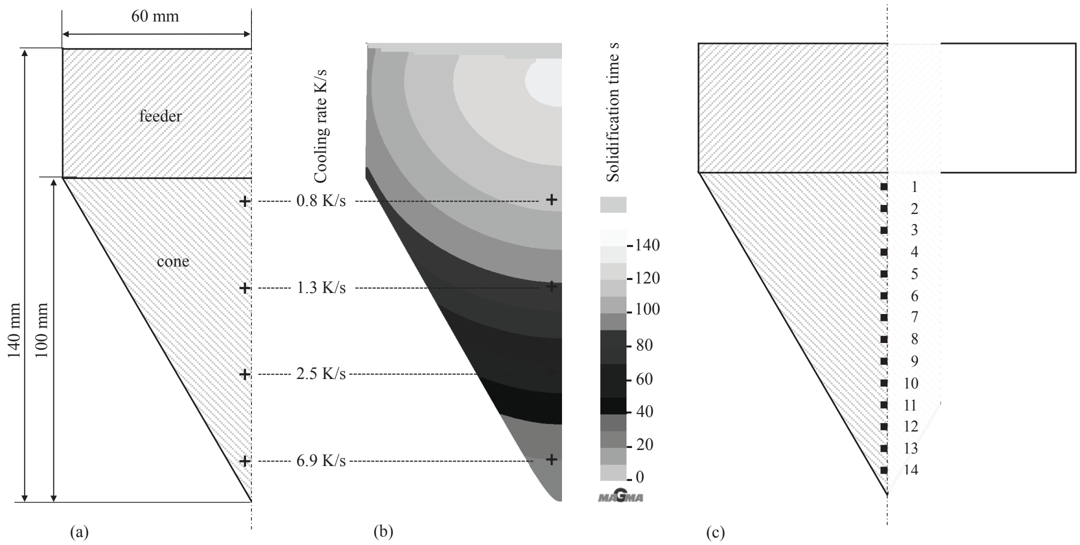

Fig. 1. (a) sample size, (b) simulation, (c) SEM measuring positions.

After machining, using abrasive paper and polish towels with a diamond suspension up to 1 µm, the material's microstructure co-linear with the cone's axis of symmetry was investigated by SEM using BSE and SE as well as metallography using bright field imaging (see Fig. 1(c)). For recording the bright field pictures the samples' surface was etched using a solution of 2 ml HCl, 3 ml HNO_3 and 95 ml C_2H_6O. Finally the samples' ferromagnetic properties were examined terms of magnetic component labeling by means of a magnetic write-head and GMR-sensor, see Fig. 2 and the material's magnetic hysteresis, more precisely by comparing the maximum energy products. The magnetic energy product is a measurement for the maximum amount of magnetic energy stored in a magnetic material and is suitable for the comparison of several industrial used magnets. It's calculated using the maximum magnetic flux density and the maximum magnetic field strength in the second quadrant of a hysteresis curve. [6]

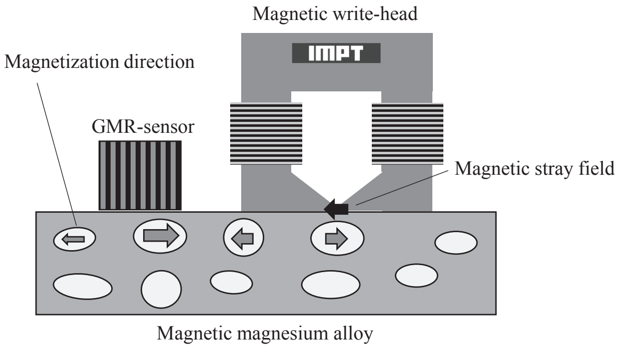

Fig. 2. Write-read-head [7].

The objective of this investigation is to compare the quality of the written labels depending on alloy composition and cooling conditions during casting. Therefore, each sample (MgCo4 and MgCo4Zn2) was labeled with the binary code "0011001100110011" by means of a write-head. The write-head's distance to the surface of the sample was 0.7 mm during the labeling process. The data track was constantly written in the direction of the axis of symmetry, and thus, along the areas of different cooling rates. These data tracks could be read out with a GMR-sensor as is explained in [7]. The results of this evaluation are measured voltages in relation to the sample's length. The orientation of the magnetization in the material causes a change in electrical resistance in the GMR-sensor, so that the measured voltage varies. If the material's magnetizability is high, the written binary zeroes and ones can be distinguished unambiguously. Depending on the magnetic remanence and the distribution of the ferromagnetic precipitates in the material, the magnetic reversals in the material, which are generated by the write-head, are stronger or weaker (see Fig. 3(b)). Each bit is 400 µm wide. In order to improve readout, each bit is written twice to enlarge the individual bit cells.

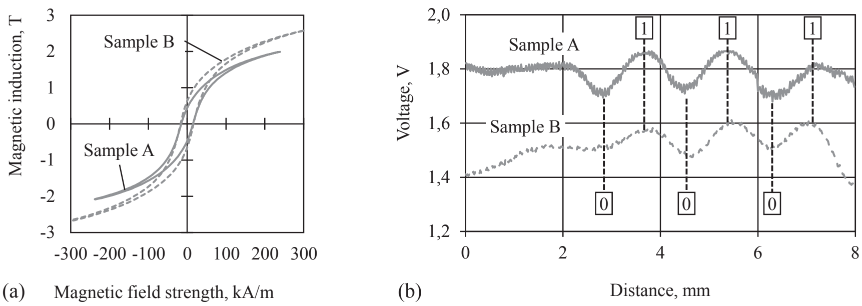

Fig. 3. (a) Magnetic hysteresis, (b) GMR-sensor's voltage curves [2].

The magnetic hysteresis of the cuboid shaped samples with dimensions of 5 mm x 5 mm x 2 mm was determined, using a vibrating sample magnetometer (EG&G Princeton Applied Research Model 4500). Four material samples of each alloy taken from the marked points in Fig. 1(a) are used to calculate the maximum energy product and to compare the energy product in terms of the cooling rate and to other industrial used magnets.

In this context no further investigations are known with regard to the investigation of magnetic magnesium based on cobalt and magnesium. However, there are industrial applications dealing with the injection molding of polymer-bounded magnetic particles to manufacture net-shaped hardmagnetic parts. [6, 8]

3. Results

3.1. Materials analysis

The quality of written data tracks was compared to the microstructure and formation of ferromagnetic Co-rich phases in the MgCo4 and MgCo4Zn2 alloys. Table 1 compares the nominal and actual alloy compositions as measured by EDX analysis. Each value represents the mean value of 14 EDX measurements (see Fig. 1(c)).

Table 1. EDX-results: MgCo4 and MgCo4Zn2 in wt.-%

Element	MgCo4 nominal	MgCo4 actual	MgCo4Zn2 nominal	MgCo4Zn2 actual
Mg	96	97.09	94	95.05
Co	4	2.91	4	3.10
Zn	-	-	2	1.85

The recording locations of the SEM and metallographic images are marked in Fig. 1(c) (points 1 – 14). Two of these locations are used to demonstrate the results exemplarily, here pt. 4 and pt. 12.

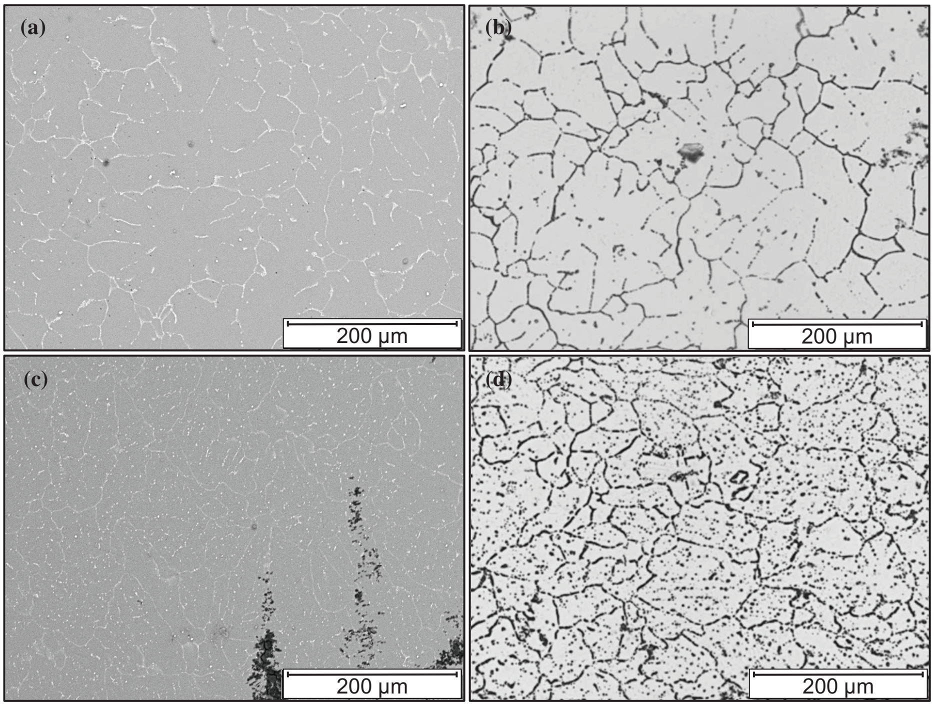

Fig. 4. MgCo4: BSE images from (a) pt. 4 and (c) pt. 12 in Fig. 1(c). The corresponding optical micrographs are shown in (b) and (d), respectively.

In Fig. 4(a/c) and Fig. 5(a/c) BSE images of casting subareas with a high and a low cooling rate are shown. The Co-rich structures are brighter due to their higher atomic number. Fig. 4(b/d) and Fig. 5 (b/d) demonstrate the corresponding areas by means of optical micrographs. In this case the Co-rich structures are darker due to the etching. The Mg-Co-compound in Fig. 4 indicates a finely dispersed structure of Co-rich eutectic precipitations in the areas of the inter-dendritic network and at the grain boundaries. Due to the different cooling rates in Fig. 4(a/b) and Fig. 4(c/d), a more dense segregation structure is recognizable. Hence, in areas of higher cooling rates, the Co-rich structures are distributed more densely on the sample surface.

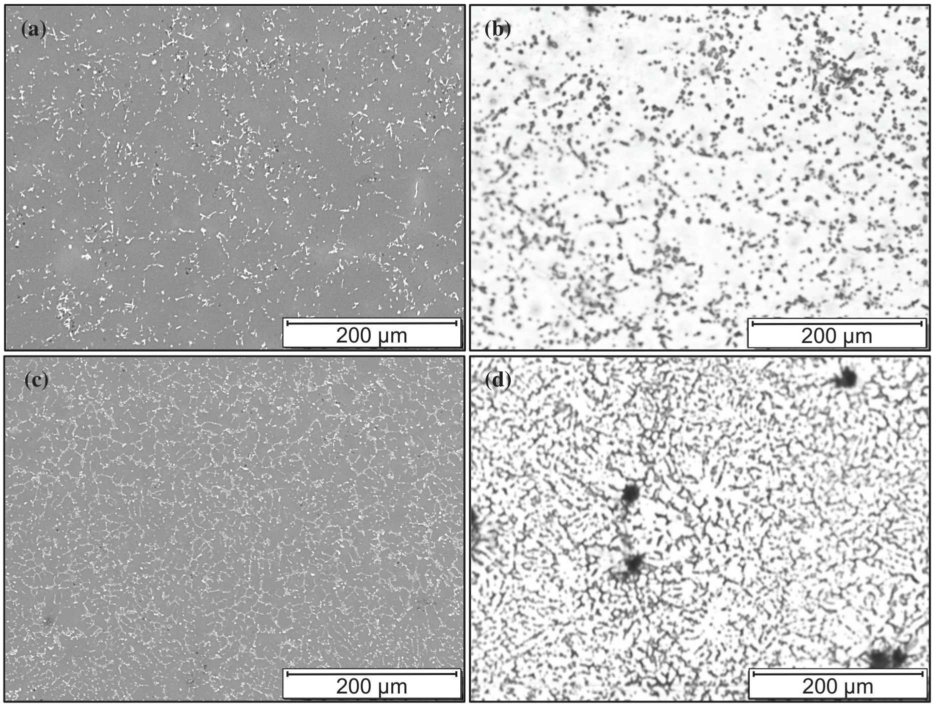

Fig. 5. MgCo4Zn2: BSE images from (a) pt. 4 and (c) pt. 12 in Fig. 1(c). The corresponding optical micrographs are shown in (b) and (d), respectively.

With the addition of Zn, the microstructure changed (see Fig. 5). The amount and continuity of the Mg-Co-Zn-compound is increased. However, the grain-size depends on the cooling rate, too.

3.2. Data storage

Using the magnetic write-head (see Fig. 2) the binary data track was written to the samples surface in the areas in Fig. 4 and Fig. 5. Therefore, it is possible to compare the alloys' microstructures and the read out quality of the magnetic labeling.

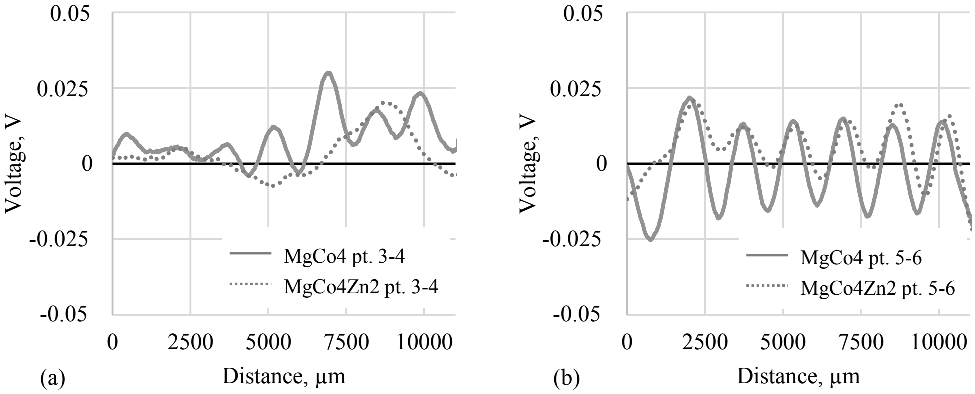

Fig. 6. Voltage-distance-diagram (a) areas 3-4 (b) areas 5-6.

In Fig. 6 the GMR-sensor's voltage and the measurement distance are shown. The originally measured voltage curves were mean-shifted to the y-axis for a better comparability. For the magnetic labeling a unique distinguishability of the curve's maxima and minima is required. In this work the maximum represents the binary one and the minimum represents the binary zero. At best, a sinusoidal voltage signal with a constant amplitude and without a continuous linear increasing is measured.

The measurements in Fig. 6 were made close to the cone tip with a high cooling rate and hence a small grain-size. The distinction of ones and zeroes in Fig. 6(a) MgCo4 is possible; in contrast the data track in the alloy MgCo4Zn2 is not readable. However, Fig. 6(b) shows a nearly periodic voltage curve of the alloy MgCo4 and thus an improved magnetic writability in this area. MgCo4 shows a larger amplitude than MgCo4Zn2 and therefore favorable magnetic properties in the area 5-6.

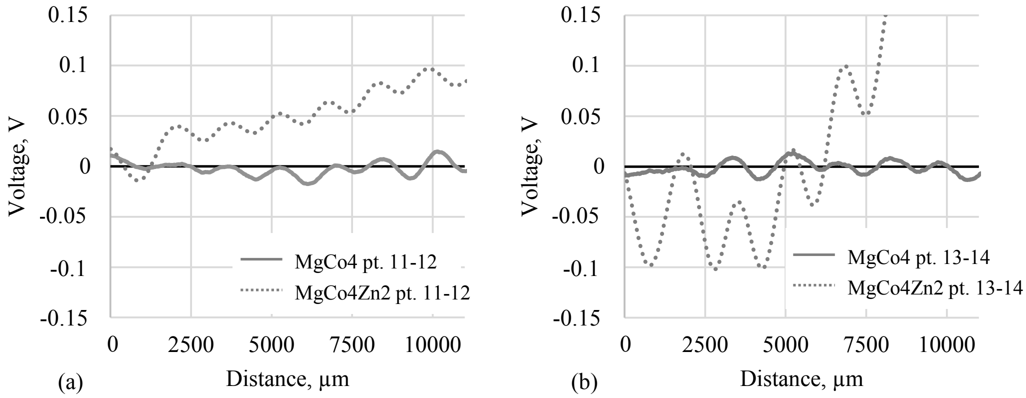

Fig. 7. Voltage-distance-diagram (a) areas 11-12 (b) areas 13-14.

The results in Fig. 7 show the corresponding values from the areas 11-14 close to the cone foot. In this location the cooling rate is lower than in area 3-6. Concerning MgCo4Zn2 in Fig. 7(a), a unique distinction between zero and one is possible. The values of the alloy MgCo4 show an irregular amplitude, but can be clearly distinguished. The measured values of MgCo4Zn2 exhibit a continuous linear increase, which is presumably based on a previous magnetization for the sample.

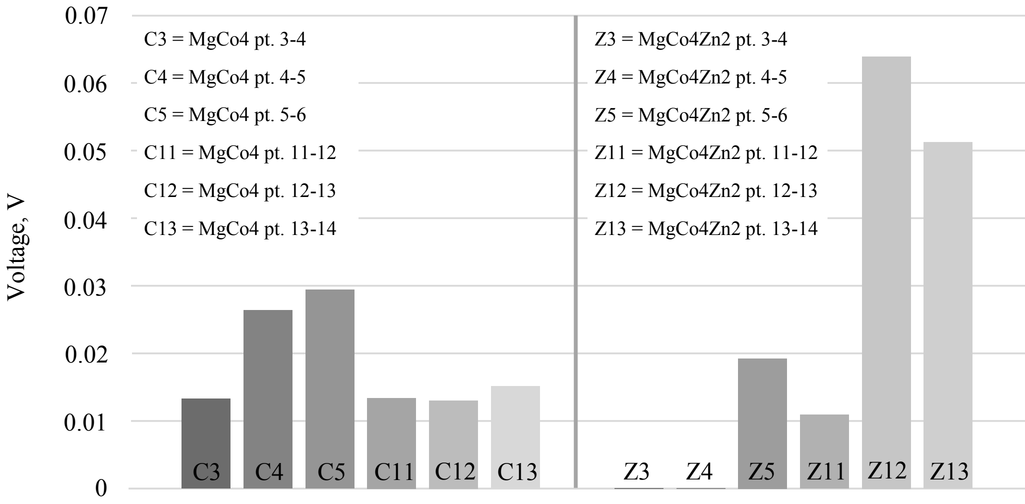

Fig. 8. Average voltage amplitudes obtained by using a GMR-sensor for MgCo4 and MgCo4Zn2.

For a better comparison, the average amplitudes for MgCo4 and MgCo4Zn2 in all areas have been summarized in Fig. 8. Each bar chart demonstrates the amplitude between the mean-minimal and mean-maximum amplitude values. The bigger the amplitude values, the better is the distinctness of the magnetic labeled binary code.

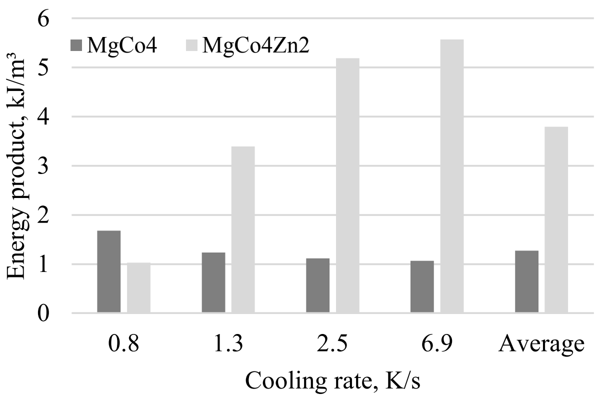

Fig. 9. Energy products of MgCo4 and MgCo4Zn2 based on hysteresis.

The magnetization quality of MgCo4 as well as MgCo4Zn2 depends on local cooling rate of the castings. Overall Z12 and Z13 in Fig. 8 show the highest amplitudes, but also a variability in the data. In this context Z3 and Z4 have no useful data tracks. By contrast, the overall voltage level of the labeling in MgCo4 is lower, but distributed more evenly depending on the range of cooling rate. In rapidly solidified areas of the MgCo4 sample the magnetic labels are superior to areas with a lower cooling rate.

The maximum energy product is helpful to arrange these results in the state of the art. Fig. 10 shows the maximum energy products of MgCo4 and MgCo4Zn2 depending to the local cooling rates. MgCo4Zn2 got a higher energy product than MgCo4 in general, except at 0.8 K/s cooling rate. Furthermore the measured values are increasing with an increasing cooling rate. In contrast, MgCo4 got decreasing energy products with increasing cooling rates. Compared to the magnetic labeling test these investigations show a similar result. In general the energy product of the MgCo4Zn2 samples is higher for larger cooling rates, so the GMR-sensor's average voltage amplitude is large. Nevertheless it should be noted that the quality of the labeled binary codes concerning MgCo4Zn2 has been detrimental to store data and read again. In contrast, MgCo4 allows a readable data storage but with a diminished degree of measured values.

Table 2. Maximum energy products of common magnet materials [6] compared to MgCo4 and MgCo4Zn2 as cast.

Magnetic material	MgCo4 (average cooling rate)	MgCo4Zn2	BaFe	SrFe	AlNiCo	SmCo	NdFeB
Energy product, kJ/m³	1.3	3.8	30	35	80	240	340

To compare the magnetic properties of the alloys determined in this work to other industrial used magnet materials the maximum magnetic energy product, shown in Table 2, is suitable. It can be recognized that the industrial magnets have larger energy products and therefore considerably more distinctive hardmagnetic qualities.

4. Conclusion

In this work the magnetic labeling quality as a function of local cooling rates in MgCo4 and MgCo4Zn2 cone-shaped castings has been investigated. First the alloys' microstructures have been analyzed using SEM and optical micrographs. In order to compare these pictures with the quality of the labeled data track a binary code was written in the corresponding areas using a magnetic write-head. A GMR-sensor was used in order to read out the data tracks and to compare their quality based on the measured voltage curves. The ternary alloy MgCo4Zn2 seems to be less suitable for magnetic labeling than the binary alloy MgCo4. However, MgCo4Zn2 has got favorable mechanical properties in contrast to MgCo4 (see [2]). In conclusion, a faster solidification favors the material-inherent data storage using MgCo4.

5. Acknowledgements

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